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CRYSTAL STRUCTURE OF PHENANTHRENE

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ABSTRACT: The crystal structure of phenanthrene has been determined by the help of Fourier synthesis method. Integrated intensities of a large number of axial and prism planes were determined from oscillation, rotation and moving film photographs and absolute values of structure factors were determined by comparison with aluminium. On the basis of these *F*-values and existing chemical physical and magnetic data, a structure is found out by trial-and-error method. Electron density projection map on the (010) face shows the picture of the molecule quite clearly. The length of one of the molecules makes an angle of 75° with the *a*-axis and 6° with the (010) plane and the plane of the molecule is inclined at 60° to the (010) plane. The orientation of the second molecule is governed by the twofold screw axis. A three dimensional Fourier summation to give out the detailed structure analysis is in progress.

The crystalline structure of phenanthrene was studied by the X-ray diffraction method previously by Mark and Hengstenberg (1929), who found the following dimensions for the unit cell

$$a = 8.60\text{Å} \qquad b = 6.11\text{Å}$$

$$c = 19.24\text{Å} \qquad \beta = 81°45'$$

with 4 molecules in the unit cell. From a study of systematic absent planes they assigned the space-group C_{2h}^5—$P2_1/c$ in the monoclinic system to this crystal. We have taken up a complete structure determination of this crystal on account of its importance in the domain of organic chemistry. From over-exposed rotation photographs and goniometric measurements, it was found out that the actual c^1 axial length of the unit cell was really half the value found out by Mark and Hengstenberg with the following values for axial lengths and angles

$$a = 8.57\text{Å} \qquad b = 6.11\text{ Å}$$

$$c = 9.47\text{Å} \qquad \beta = 82°30'$$

No. of molecules in the unit cell = 2.

From an examination of intensities of the (*h*0*k*) planes and from steric and symmetry considerations, the crystal was classified as belonging to the space group C_2^2—$P2_1$ in the monoclinic crystal class (Basak, 1948).

Oscillation and moving film pictures about the three crystallographic axes were next recorded. The estimated intensities of the different planes

by comparison with a logarithmic sector wedge were converted to absolute intensities and thence to absolute values of structure factors by matching some of the reflections with standard aluminium powder lines.

In carrying out a two dimensional Fourier summation, the phases of the structure factor terms were determined by the conventional method of trial-and error. The already existing chemical, magnetic and other data were utilised for narrowing out the field over which trials were to be given From the magnetic measurements of Krishnan a d Banerjee (1936), the molecular orientation in the phenanthrene crystal, assuming a planar configuration of the molecule, comes out to be as follows : The length of the molecule lies in the (010) plane at 78 5° with the *a*-axis. On the basis of their corrected values for magnetic data, we have made fresh calculations and the inclination of the molecular plane to the (010) crystallographic plane comes

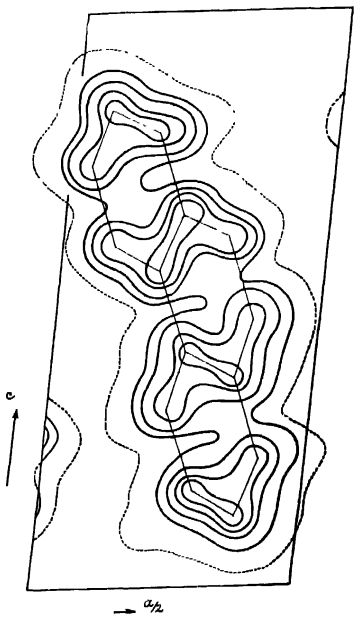

FIG. 1

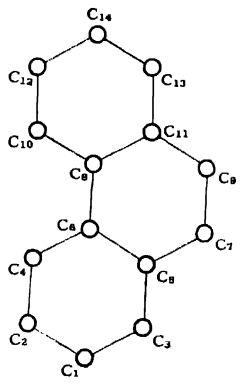

FIG. 2

out to be nearly 60° By far the strongest reflection happens to be from the (201) crystallographic plane; the measured absolute value of structure factor being about 61% of that had all the atoms been on the (201) plane. The (211) plane too is strong enough, suggesting that the inclination of the molecular plane to the (010) plane is near about 60°. Moreover the crystal has got a very prominent cleavage along the (201) plane. Taking all these

TABLE I
(Part I)

Index of the spot	*F* Calculated	*F* Observed	Index of the spot	*F* Calculated	*F* Observed
001	−36	35	201	+57	68
002	−19	24	202	−2	6
003	−11	15	203	0	abs
004	−16	30	204	−3	3
005	+13	19	205	−1	5
006	−1	1	206	−2	1
007	+3	abs	207	+3	abs
008	0	abs	208	−6	3
009	−1	1	209	+2	2
00(10)	0	abs	$20\bar{1}$	−17	18
100	+1	1	202	−9	11
200	−25	30	203	−15	20
300	+13	14	$20\bar{4}$	+25	33
400	−5	4	$20\bar{5}$	−4	abs.
500	+7	7	206	−2	1
600	−4	4	207	−2	2
700	−5	7	$20\bar{8}$	+4	7
800	0	abs	209	−2	2
900	−1	abs	301	+7	5
101	−8	abs	302	−1	1
102	−19	20	303	−3	abs
103	+2	4	304	−11	6
104	−2	4	305	−3	2
105	+7	5	306	−3	abs
106	+5	5	307	+2	1
107	+4	abs	308	+15	11
101	+5	12	309	−6	4
$10\bar{2}$	0	2	$30\bar{1}$	−5	5
$10\bar{3}$	0	abs	302	0	[illegible]
$10\bar{4}$	+14	7	303	+5	2
$10\bar{5}$	−3	abs.	304	−8	3
$10\bar{6}$	−6	5	$30\bar{5}$	+1	3

TABLE I(*contd.*)

Index of the spot	*F* Calculated	*F* Observed	Index of the spot	*F* Calculated	*F* Observed
307	+4	abs	306	+2	abs.
307	+4	abs	509	+1	abs
308	−6	abs	601	+1	abs.
309	+1	abs	602	+3	3
401	+1	4	603	−3	3
402	−5	5	604	+1	abs
403	+6	6	605	−3	−3
404	0	6	601	−1	abs.
405	0	abs	602	−1	abs
406	+2	abs	603	+4	4
407	0	2	604	+3	3
408	+5	3	605	+2	abs
401	−6	5	701	+11	9
402	−5	4	702	−2	abs
403	+11	7	703	−3	abs
404	+1	abs	704	−1	abs
405	−5	abs	705	+7	7
406	+2	abs	706	−4	3
407	+6	4	701	−2	abs
408	−4	2	702	−2	abs
501	0	1	703	−4	3
502	−3	abs.	704	+5	7
503	+2	abs	705	−1	abs
504	+12	12	706 −	0	abs.
505	−11	9			
509	+10	12			
501	−3	2			
502	−3	1			
503	−2	abs.			
504	+3	abs.			
505	−3	abs.			

TABLE I (Part II)

Since in these projections, there are no centres of symmetry, only the numerical values of F are given

Index of the plane	F Calculated	F Observed	Index of the plane	F Calculated	F Calculated
020	16	18	110	41	46
040	3	3	210	30	38
060	5	9	310	1	6
011	7	4	410	10	20
012	3	abs.	510	12	11
013	6	abs.	610	5	6
014	11	14	710	2	abs
015	10	15	130	5	4
016	2	abs	220	8	5
017	8	7	320	12	14
021	11	15	420	5	4
022	11	24	520	8	7
023	13	19	620	2	abs.
024	4	6	130	4	4
025	3	abs	230	7	7
026	2	abs	330	3	abs.
027	11	14	150	5	9
031	10	5			
032	6	abs			
033	9	9			
034	1	abs.			

TABLE II

Co-ordinates of the atoms

Description of the atom	x/a	y, b	
C_1	0·3850	0·3100	0·1100
C_2	0·2920	0·1249	0·1538
C_3	0·4148	0·4700	0·2105
C_4	0·2289	0·1008	0·2980
C_5	0·3517	0·4469	0·3547
C_6	0·2587	0·2618	0·3985
C_7	0·3815	0·6079	0·4552
C_8	0·1956	0·2377	0·5427
C_9	0·3184	0·5838	0·5994
C_{10}	0·1026	0·0526	0·5865
C_{11}	0·2254	0·3987	0·6432
C_{12}	0·0395	0·0285	0·7307
C_{13}	0·1623	0·3746	0·7874
C_{14}	0·0693	0·1895	0·8312

points into consideration, the molecule is assumed to be oriented with its length in the (010) plane at $78\frac{1}{2}°$ to the a-axis and its molecular plane at 60° to the b-plane. Trials were given by varying the orientations and matching the calculated values of structure factors with the observed ones. The lengths of the aromatic c-c bond were assumed to be 1·41 Å in conformity

with the determinations of similar compounds by Banerjee (1930), Robertson (1933) and others.

After a large number of trials, agreement between observed and calculated F-values was reached at the following orientation . The length of the molecule which itself is planar makes an angle of 6° with the b-plane and 75° with the a-axis while molecular plane is inclined at 60° to the (010) plane. The orientation of the second molecule in the crystal is governed by the two-fold screw axis of symmetry.

A two-dimensional Fourier summation was next carried out around b-axis using the method of summation described by Lipson and Beevers (1934). From the resultant electron density map the appearance of the molecule can be seen with reasonable clearness.

The x-and z-co-ordinates only are obtained from this projection, while the y-co-ordinates were determined by trial from the F-values of the (okl) and (hko) planes. The agreement between observed and calculated values of structure factors can be seen from Table I.

Projections along the other two axes are in progress and a refinement of the parameters by a three dimensional Fourier summation will be carried out.

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